Supplementary Data

Structure-Reactivity Correlations in Nucleophilic Substitution Reactions of Y-substituted Phenyl X-substituted Benzoates with Anionic and Neutral Nucleophiles

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Table S1. Summary of kinetic data for the reaction of 4-nitrophenyl 4-dimethylaminobenzoate(**1k**) with OH⁻ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

$[OH^-] / 10^{-3}M$	$k_{obsd} / 10^{-3}s^{-1}$
17.8	2.46
32.7	4.45
45.2	6.39
56.0	7.94
65.3	9.21

$k_N = 0.144 \pm 0.002\ M^{-1}s^{-1}$

intercept = -0.0003 s^{-1} corr. coeff. = 0.9996

Table S2. Summary of kinetic data for the reaction of 4-nitrophenyl 4-hydroxybenzoate(**1l**) with OH⁻ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

$[OH^-] / 10^{-3}M$	$k_{obsd} / 10^{-4}s^{-1}$
17.8	1.60
32.7	3.11
45.2	4.43
56.0	5.45
65.3	6.40

$k_N = 0.0101 \pm 0.0001\ M^{-1}s^{-1}$

intercept = -0.00001 s^{-1} corr. coeff. = 0.9997

Table S3. Summary of kinetic data for the reaction of 4-nitrophenyl 3,5-dinitrobenzoate(**1a**) with CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-1}s^{-1}
0.748	0.314
1.49	0.640
2.23	0.975
2.96	1.26
3.68	1.56

k_N = 42.5 ± 0.6 M^{-1}s^{-1}

intercept = 0.0006 s^{-1} corr. coeff. = 0.9999

Table S4. Summary of kinetic data for the reaction of 4-nitrophenyl 4-chloro-3-bromobenzoate(**1b**) with CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-2}s^{-1}
1.61	1.33
3.19	2.69
4.75	4.03
6.28	5.08
7.79	6.45

k_N = 8.17 ± 0.17 M^{-1}s^{-1}

intercept = 0.0006 s^{-1} corr. coeff. = 0.9993

Table S5. Summary of kinetic data for the reaction of 4-nitrophenyl 4-nitrobenzoate(**1c**) with CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-2}s^{-1}
3.97	2.55
7.79	4.69
11.5	7.29
15.0	9.27
18.4	11.5

k_N = 6.25 ± 0.12 M^{-1}s^{-1}

intercept = -0.0002 s^{-1} corr. coeff. = 0.9993

Table S6. Summary of kinetic data for the reaction of 4-nitrophenyl 4-cyanobenzoate(**1d**) with CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-2}s^{-1}
6.03	3.10
7.80	3.85
15.0	6.80
21.7	10.2
27.9	12.8

k_N = 4.47 ± 0.08 M^{-1}s^{-1}

intercept = 0.003 s^{-1} corr. coeff. = 0.9993

Table S7. Summary of kinetic data for the reaction of 4-nitrophenyl 3-chlororbenzoate(**1e**)

with CN^{-} in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN^{-}] / 10^{-3}M	k_{obsd} / 10^{-2}s^{-1}
7.80	1.03
9.65	1.29
18.4	2.44
26.4	3.48
33.8	4.52

k_N = 1.33 ± 0.01 M^{-1}s^{-1}

intercept = -0.00007 s^{-1} corr. coeff. = 0.9999

Table S8. Summary of kinetic data for the reaction of 4-nitrophenyl 4-chlorobenzoate(**1f**)

with CN^{-} in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN^{-}] / 10^{-3}M	k_{obsd} / 10^{-2}s^{-1}
9.65	0.611
18.4	1.18
26.4	1.71
33.8	2.15
37.2	2.34

k_N = 0.628 ± 0.001 M^{-1}s^{-1}

intercept = 0.0002 s^{-1} corr. coeff. = 0.9996

Table S9. Summary of kinetic data for the reaction of 4-nitrophenyl benzoate(**1g**) with CN$^-$

in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
18.2	4.99
26.1	6.96
33.3	8.48
40.0	9.99
46.1	11.4

k_N = 0.228 ± 0.003 M^{-1}s^{-1}

intercept = 0.0009 s^{-1} corr. coeff. = 0.9996

Table S10. Summary of kinetic data for the reaction of 4-nitrophenyl 3-methylbenzoate(**1h**)

with CN$^-$ in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-2}s^{-1}
57.6	1.23
71.3	1.47
83.2	1.74
99.8	2.02
116	2.33

k_N = 0.189 ± 0.004 M^{-1}s^{-1}

intercept = 0.001 s^{-1} corr. coeff. = 0.9997

Table S11. Summary of kinetic data for the reaction of 4-nitrophenyl 4-methylbenzoate(**1i**) with CN$^-$ in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
32.6	3.68
49.9	5.85
64.7	7.64
77.5	8.89
83.2	9.70

k_N = 0.117 ± 0.003 M^{-1}s^{-1}

intercept = -0.00007 s^{-1} corr. coeff. = 0.9991

Table S12. Summary of kinetic data for the reaction of 4-nitrophenyl 4-methoxybenzoate(**1j**) with CN$^-$ in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
71.3	3.84
83.2	4.42
99.8	5.23
116	5.97
133	6.66

k_N = 0.0460 ± 0.001 M^{-1}s^{-1}

intercept = 0.0006 s^{-1} corr. coeff. = 0.9993

Table S13. Summary of kinetic data for the reaction of 4-nitrophenyl 4-dimethylaminobenzoate(**1k**) with CN$^-$ in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-5}s^{-1}
54.0	6.49
86.4	15.1
108	20.7
130	26.7

k_N = (2.65 ± 0.02) x 10^{-3} M^{-1}s^{-1}

intercept = -0.00008 s^{-1} corr. coeff. = 0.9999

Table S14. Summary of kinetic data for the reaction of 4-nitrophenyl 4-hydroxybenzoate(**1l**) with CN$^-$ in 80 mol % H$_2$O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-5}s^{-1}
108	3.26
130	3.99
162	5.20
180	5.80

k_N = (3.57 ± 0.07) x 10^{-4} M^{-1}s^{-1}

intercept = -0.000006 s^{-1} corr. coeff. = 0.9997

Table S15. Summary of kinetic data for the reaction of 4-nitrophenyl 3,5-dinitrobenzoate(**1a**) with piperidine in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[piperidine] / 10^{-3}M	k_{obsd} / $10^{-2}s^{-1}$
0.845	4.19
1.68	8.08
2.51	11.9
3.34	16.0
4.16	19.9

k_N = 47.5 ± 0.3 $M^{-1}s^{-1}$

intercept = 0.001 s^{-1} corr. coeff. = 0.9999

Table S16. Summary of kinetic data for the reaction of 4-nitrophenyl 4-chloro-3-bromobenzoate(**1b**) with piperidine in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[piperidine] / 10^{-3}M	k_{obsd} / $10^{-2}s^{-1}$
0.845	1.88
1.68	3.79
2.51	5.67
3.34	7.58
4.16	9.54

k_N = 23.1 ± 0.1 $M^{-1}s^{-1}$

intercept = -0.0009 s^{-1} corr. coeff. = 0.9999

Table S17. Summary of kinetic data for the reaction of 4-nitrophenyl 4-dimethylaminobenzoate(**1k**) with piperidine in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[piperidine] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
19.3	5.12
35.3	9.30
48.9	12.6
60.6	15.7
70.7	18.5

k_N = 0.259 ± 0.003 M^{-1}s^{-1} intercept = 0.0001 s^{-1} corr. coeff. = 0.9995

Table S18. Summary of kinetic data for the reaction of 4-nitrophenyl 4-hydroxybenzoate(**1l**) with piperidine in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[piperidine] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
19.3	1.37
35.3	2.48
48.9	3.33
60.6	4.11
70.7	4.77

k_N = 0.0659 ± 0.0006 M^{-1}s^{-1} intercept = 0.0001 s^{-1} corr. coeff. = 0.9999

Table S19. Summary of kinetic data for the reaction of 3,4-dinitrophenyl benzoate(**2a**) with CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at $25.0 \pm 0.1°C$.

$[CN^-] / 10^{-3}M$	$k_{obsd} / 10^{-2}s^{-1}$
8.68	1.71
16.7	3.36
24.2	4.81
31.1	6.08
37.6	7.28

$k_N = 1.92 \pm 0.02$ M^{-1}s^{-1}

intercept = 0.001 s^{-1} corr. coeff. = 0.9999

Table S20. Summary of kinetic data for the reaction of 4-nitrophenyl benzoate(**2b**) with CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at $25.0 \pm 0.1°C$.

$[CN^-] / 10^{-3}M$	$k_{obsd} / 10^{-3}s^{-1}$
18.2	1.92
33.3	8.74
46.1	11.3
57.1	14.0
66.6	16.2

$k_N = 0.231 \pm 0.001$ M^{-1}s^{-1}

intercept = 0.0008 s^{-1} corr. coeff. = 0.9991

Table S21. Summary of kinetic data for the reaction of 4-formylphenyl benzoate(**2d**) with

CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
18.2	2.17
33.3	3.86
46.1	5.20
57.1	6.26
66.7	7.18

$k_N = 0.103 \pm 0.002$ M^{-1}s^{-1}

intercept = 0.0004 s^{-1} corr. coeff. = 0.9997

Table S22. Summary of kinetic data for the reaction of 4-acetylphenyl benzoate(**2e**) with

CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
36.3	3.13
49.9	4.19
61.4	5.04
71.3	5.83

$k_N = 0.0768 \pm 0.0007$ M^{-1}s^{-1}

intercept = 0.0003 s^{-1} corr. coeff. = 0.9999

Table S23. Summary of kinetic data for the reaction of 3-nitrophenyl benzoate(**2g**) with

CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

$[CN^-] / 10^{-3} M$	$k_{obsd} / 10^{-3} s^{-1}$
53.5	7.70
68.1	9.73
80.3	11.4
90.5	12.9
99.4	14.2

$k_N = 0.141 \pm 0.001 \ M^{-1} s^{-1}$

intercept = 0.0001 s^{-1} corr. coeff. = 0.9998

Table S24. Summary of kinetic data for the reaction of 3-acetylphenyl benzoate(**2h**) with

CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

$[CN^-] / 10^{-3} M$	$k_{obsd} / 10^{-3} s^{-1}$
53.0	1.90
67.5	2.39
79.5	2.81
89.7	3.21
98.4	3.52

$k_N = 0.0359 \pm 0.0006 \ M^{-1} s^{-1}$

intercept = -0.00002 s^{-1} corr. coeff. = 0.9996

Table S25. Summary of kinetic data for the reaction of phenyl benzoate(**2j**) with CN⁻ in 80

mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

$[CN^-]$ / 10^{-3}M	k_{obsd} / 10^{-3}s^{-1}
52.0	5.31
66.2	6.63
78.0	7.94
88.0	8.92
96.6	9.81

$k_N = 0.0102 \pm 0.0002$ M^{-1}s^{-1}

intercept = -0.000002 s^{-1} corr. coeff. = 0.9996

Table S26. Summary of kinetic data for the reaction of 4-methylphenyl benzoate(**2k**) CN⁻ in

80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1°C.

$[CN^-]$ / 10^{-3}M	k_{obsd} / 10^{-4}s^{-1}
52.0	4.19
66.2	5.35
78.0	6.24
88.0	7.02
96.6	7.70

$k_N = (7.83 \pm 0.06)$ x 10^{-3} M^{-1}s^{-1}

intercept = 0.00001 s^{-1} corr. coeff. = 0.9999

Table S27. Summary of kinetic data for the reaction of 4-methoxyphenyl benzoate(**2l**) with

CN$^-$ in 80 mol % H_2O / 20 mol % DMSO at $25.0 \pm 0.1°C$.

[CN$^-$] / 10^{-3}M	k_{obsd} / 10^{-4}s^{-1}
52.0	4.35
66.2	5.46
78.0	6.54
88.0	7.33
96.6	8.10

$k_N = (8.43 \pm 0.01)$ x 10^{-3} M^{-1}s^{-1}

intercept = -0.000006 s^{-1} corr. coeff. = 0.9996

Table S28. Summary of kinetic data for the reaction of 3,4-dinitrophenyl benzoate(**2a**) with

hydrazine in 80 mol % H_2O / 20 mol % DMSO at $25.0 \pm 0.1°C$.

[hydrazine] / 10^{-3}M	k_{obsd} / 10^{-1}s^{-1}
4.90	1.53
9.80	3.11
14.7	4.77
19.6	6.44
24.5	7.97

$k_N = 33.1 \pm 0.2$ M^{-1}s^{-1}

intercept = -0.009 s^{-1} corr. coeff. = 0.9999

Table S29. Summary of kinetic data for the reaction of 3,4-dinitrophenyl benzoate(**2a**) with glycylglycine in 80 mol % H_2O / 20 mol % DMSO at $25.0 \pm 0.1°C$.

[glycylglycine] / $10^{-3}M$	k_{obsd} / $10^{-3}s^{-1}$
3.77	5.82
7.26	11.0
10.5	15.7
13.5	20.1
16.3	24.5

$k_N = 1.48 \pm 0.01 \ M^{-1}s^{-1}$

intercept $= 0.00002 \ s^{-1}$ corr. coeff. $= 0.9999$